Synthesis and Characterisation of Carbon Nanotube Reinforced Hydroxyapatite Ceramics for Biomedical Applications

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CERTIFICATE OF AUTHORSHIP/ORIGINALITY

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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ABSTRACT

Reinforcement of nano-materials is important in many industrial processes, including the strengthening of biomedical implants for medical applications (for example artificial hip replacements). Human bone is mainly composed of collagen and hydroxyapatite (HAp) nanocrystals. HAp has been produced synthetically, with a structure and chemical composition almost identical to the HAp in human bone. When implanted, this synthetic material is accepted by the body. However, it has poor mechanical properties, making it unreliable for implant applications. The aim of this research is to combine biocompatible HAp with another biocompatible compound (carbon) to form a composite material with improved physical properties, including density, and strength.

The pure HAp was chemically synthesised using a precipitation reaction between calcium nitrate and diammonium hydrogenphosphate. The precipitate was centrifuged, washed and dried. After drying, the powder was heat-treated at 650 °C for 4 hours, and then hot isostatically pressed (HIP), at 100 MPa, 900 °C, in argon gas. Carbon nanotubes (CNTs) were chosen to reinforce the HAp based on their extreme flexibility and strength. Two production methods of incorporating CNT material (between 2 wt% and 10 wt% CNTs) into the HAp have been investigated: chemical precipitation reinforcement and physical reinforcement.

Full electron microscopy and diffraction characterisations of the pure and composite materials have been completed. The HIP process forms a dense pellet, with no voids between the CNT material and the HAp matrix. All CNTs imaged in the TEM had minimal degradation to the CNTs, with no visible change in the appearance. Unfortunately, the as supplied CNT material contained pockets of graphite which were non-uniformly distributed through the HAp matrix. Hence, the mixture was not homogeneous, and the CNTs were not bonding directly with the HAp. Neutron diffraction characterisation confirms that the crystal structure of the HAp was not affected by the CNT inclusion. Neutron diffraction patterns collected before and after sintering show that the CNTs must be heated in an inert atmosphere or a vacuum to prevent the CNT material from oxidising. TEM confirms no obvious visual damage to

the CNTs in the material. Neutron diffraction data have enabled the positions of the hydroxide bonds to be determined. Small-angle-neutron scattering showed that the surface morphology was rough. The CNT material dominated the neutron scattering results in the composite samples, which minimised the information obtained from the HAp matrix.

A range of physical properties of the pure HAp and the composite samples were measured. These included the density, porosity, surface area, hardness, fracture toughness, and Young's modulus. Two complementary techniques have been employed to measure the hardness; the Vickers microhardness and the Berkovich nanoindentation techniques. The density of the HIP samples of all of the materials was greater than ~94% of the theoretical density, with pure HAp materials as high as ~99%. The hardness values for the material measured by micro-indentation were quite high – either equal to or greater than the literature values. Unfortunately, this resulted in a lower fracture toughness, which was not improved by the addition of the CNTs. It is possible that, if the graphite phase were removed from the material, the fracture toughness could improve. Current CNT production methods do not allow full removal of the graphite.

Optical micrographs from the Vickers indentation tests of the composites show varying stages of lateral crack patterns formed, suggesting plastic deformation below the surface. This was consistent throughout all samples. The results from nanoindentation of the bulk material showed that, overall, the samples with the CNT material had a lower Young's modulus than the pure HAp samples (for both the laboratory synthesised and the commercial material). The microhardness and nanoindentation work showed that all of the samples were influenced by an indentation size effect, where the hardness decreased with increasing load.

Further work for increased fracture toughness in these composites requires the production of a pure CNT material (with no graphite impurity) for incorporation with the HAp. It is possible that, without the graphite impurity to bind the CNTs, they will spread more homogeneously throughout the HAp matrix, and bond along the CNT length. No pure CNT material was commercially available at the time of submission of this thesis.

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